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PHYSICAL CHEMISTRY OF TETRAKIS(DIMETHYLAMINO)ETHYLENE.

III. CHEMILUMINESCENCE QUANTUM YIELD AT 30°C

by

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ABSTRACT. The chemiluminescence quantum yield for a
n-decane solution of tetrakis(dimethylamino)ethylene
(TMAE), oxygen, and 1-octanol at 30°C was determined
under a wide range of experimental conditions. It
is found that a maximum possible quantum yield of
3.6% can be expected. The yield is found to depend
upon $TMAE/[11.5(TMAE) + 1]$ so that it decreases with
decreasing TMAE concentration. A discussion is
given concerning yields reported by other workers.

U.S. NAVAL ORDNANCE TEST STATION
China Lake, California   April 1966

FOREWORD

This report covers a portion of the work performed at this Station on the chemiluminescence of tetrakis(dimethylamino)ethylene (TMAE).

It has been common practice to measure "average" chemiluminescence quantum yields in terms of total light emitted for the amount of material consumed in the course of the reaction. In the case of TMAE, the quantum yield depends on so many parameters that a single "average" value has little scientific value. The work reported here shows how precise measurements can yield an accurate chemiluminescence quantum yield that is applicable over a wide range of experimental conditions.

This work was initiated in January 1965 under Bureau of Naval Weapons Task Assignment RMMO 32-024/216-1/F008-17-02. The work was completed in February 1966 with the last month being supported under Army-Picatinny Arsenal MIPR-No. 6311-1017.

This report is transmitted for information only. It presents information released at the working level that is still subject to modification and withdrawal.

Released by
WILLIAM S. McEWAN, Head
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28 February 1966

Under authority of
HUGH W. HUNTER, Head
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CONTENTS

ACKNOWLEDGMENT

NOMENCLATURE

A_0 Formal concentration of the 1-octanol added to the n-decane without consideration of polymerization, mole liter^{-1}

A_1 Concentration of the 1-octanol monomer, mole liter^{-1}

A_4 Concentration of the 1-octanol tetramer, mole liter^{-1}

B Area of spherical mirror, cm^2

CQY   Chemiluminescence quantum yield, einstein mole^{-1}

C_λ Phototube calibration constant at wavelength λ, photon sec^{-1} amp^{-1}nm^{-1}

c Aperture area in mm^2

d Distance of spherical mirror from aperture, cm

dx Derivative of x

E Concentration of TMAE, mole liter^{-1}

einstein   One mole of photons (6.03×10^{23} photons)

$F(A)$ Rate function for the autoxidation of TMAE that contains all constants and terms related to the species of alcohol present

F_λ Spectral radiant flux, photon sec^{-1} nm^{-1}

h_λ Height of emission curve at wavelength λ

I Light intensity, einstein sec^{-1} liter^{-1}

i Variable indicating some specific species or item

J_t Factor relating phototube calibration (specific to TMAE) variation with time of a measurement, t

K_i Stern-Volmer quenching constant for quenching agent i, liter mole^{-1} (except for oxygen where it is torr^{-1})

K_t Phototube calibration specific to emission of TMAE at time t

L Term containing all constants other than rate and quenching terms in light kinetics expression for low TMAE concentrations, einstein mole^{-2} liter

$\underline{M}$ Molar, mole liter^{-1}

M_λ Reflectance of mirror system at wavelength λ

n Number of paired values of datum used in a calculation

nm Nanometer (1 nm = 1 mμ)

P Normalizing function

PMC Photomultiplier current

PMCF Photomultiplier current at reference voltage F

P_{O_2} Oxygen pressure in torr

Q_i Concentration of quenching agent i, mole liter^{-1}

R Instrument reading

R_λ Phototube response at wavelength λ, amp sec nm photon^{-1}

r Reference

s Sample

T Transmittance

t Day of test (Jan 1, 1965 = day 1)

TMAE Tetrakis(dimethylamino)ethylene

torr Pressure unit (1 torr = 1 mm of mercury)

V_i Photomultiplier current at reference voltage F(836 volts)/ photomultiplier current at voltage i

W.L. Working lamp

η_i Index of refraction of medium i

λ Wavelength

Φ_c Chemical efficiency term, moles excited species formed for each mole of reacted TMAE in unit time

Φ_e Emission quantum yield that includes effect of quenchers, einstein mole^{-1}

Φ_o Photoluminescence quantum yield in n-decane without added quenching materials, einstein mole^{-1}

ψ Angle from perpendicular to surface

INTRODUCTION

In a previous report (Ref. 1), it was shown that the chemiluminescence quantum yield (CQY) of tetrakis(dimethylamino)ethylene (TMAE) was dependent upon the concentration of the TMAE. A year later, Winberg, Downing, and Coffman (Ref. 2) as well as Paris (Ref. 3) gave values for the CQY of TMAE without evaluating the concentration effect. By the very lack of experimental detail of their reports, it must be assumed that the values presented by these authors were intended to be only very rough approximations.

It is the purpose of this report to show, in detail, our experimental method for the determination of the CQY of TMAE and to compare these results to those measured by Winberg et al. and Paris. These systems will be discussed so that the reader may be able to have some degree of evaluation of the techniques employed.

For a chemiluminescent system in which steady-state conditions exist between the reactants and the formation of a single electronically excited light emitting species:

$$I = \phi_e \times \phi_c \times \left(- \frac{d[\text{reactant}]}{dt} \right) \tag{1}$$

where

I = light intensity in einsteins liter^{-1} sec^{-1}

ϕ_c = chemical efficiency in terms of moles of electronically excited species for each mole of reactant that was consumed per second

ϕ_e = emission quantum yield in terms of einsteins (or moles of photons) emitted for each mole of excited product

$d[\text{reactant}]/dt$ = rate of reaction of one of the starting materials, mole liter^{-1} sec^{-1}

The emission quantum yield term can be expanded by the use of Stern-Volmer quenching constants:

$$\phi_e = \frac{\phi_0}{1 + \Sigma K_i [Q_i]} \tag{2}$$

where

ϕ_O = photoluminescence quantum yield in solution but without the effect of added quenchers, Q

K_i = Stern-Volmer quenching constants, usually in terms of liter mole^{-1}

$[Q_i]$ = concentration of light quenching agent i

The equations above are presented in greater detail in a report (Ref. 4) describing a portion of our work presented at the Chemiluminescence Symposium at Durham, North Carolina in April 1965. They are included here for the convenience of the reader. A detailed account of our measurements of ϕ_O was recently reported (Ref. 5). Using the chemiluminescence Stern-Volmer quenching constants that were reported at Durham, with the value of ϕ_O,

$$\phi_e = \frac{0.35}{1 + 48A_1 + 1040A_4 + 0.085P_{O_2}} \tag{3}$$

$$A_O = A_1 + 4A_4 \tag{4}$$

$$A_4/(A_1)^4 = 780 \tag{5}$$

where

A_O = molar concentration of 1-octanol added to the system

A_1 = molar concentration of 1-octanol monomer

A_4 = molar concentration of 1-octanol tetramer

P_{O_2} = oxygen pressure in torr

It has already been shown how it is possible to measure d(TMAE)/dt (Ref. 6). Through evaluation of the kinetics of light emission (Ref. 1), it was found that the light intensity varied with the square of the TMAE concentrations for TMAE less than 10^{-2} $\underline{M}$. Paris (Ref. 3) also found this for a methanol-cyclohexane system. Since d(TMAE)/dt was only first order in TMAE concentrations, then ϕ_c must be proportional to the TMAE concentration (Ref. 1 and 7).

In the present report, the light kinetics will be evaluated at higher concentrations of TMAE, and it will be shown that ϕ_c does not involve any parameters other than the TMAE concentration. By measurement of the absolute intensity of light, the constants relating to ϕ_c will be determined by means of Eq. 1. This measurement will allow the determination of the CQY, which is $\phi_e \times \phi_c$ of Eq. 1.

EXPERIMENTAL

EQUIPMENT AND CHEMICALS

The system for the use of a tungsten lamp as a radiation source was constructed following the guidelines recommended by Stair, et al. (Ref. 8). Since it was necessary to exclude all light other than that of the lamp, all of the system except for the lamp was placed in light-tight enclosure as shown in Fig. 1. Flock paper and light baffles were placed in the $1-^3/_4$-inch diameter tube connecting the lamp and the photometry box.
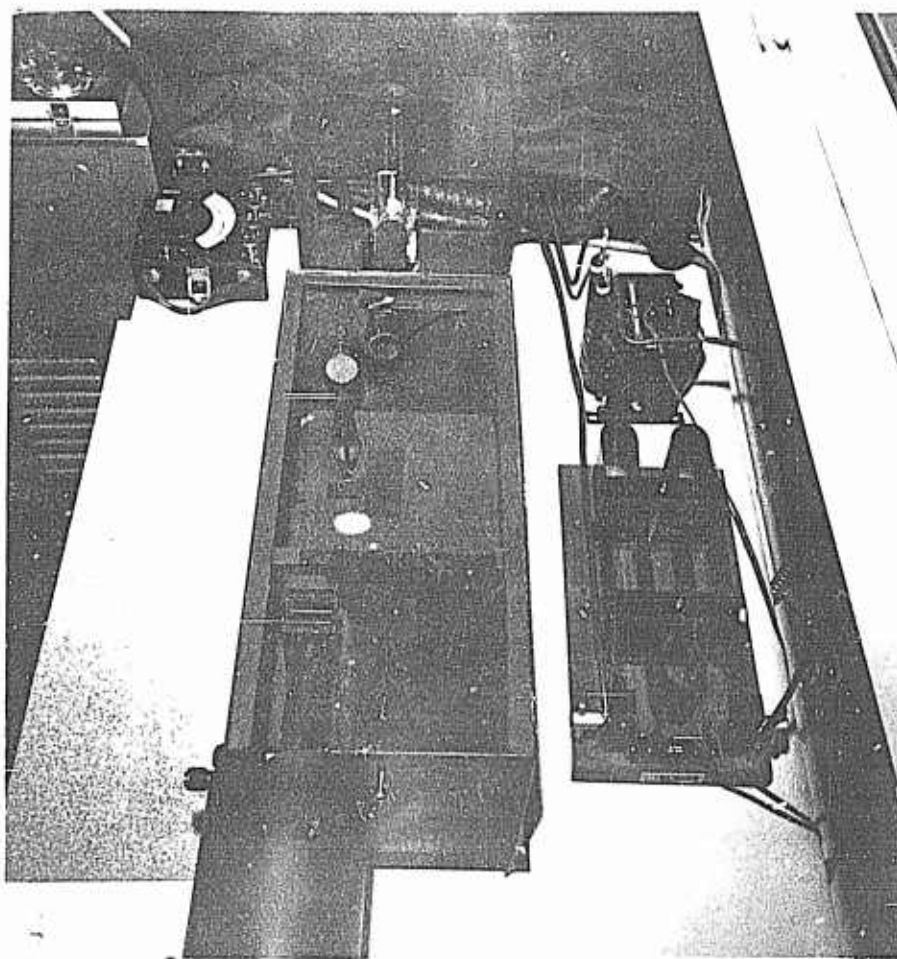
FIG. 1. Photometry Box

The statistics of the optical equipment are as follows:

Lamp, 30 amperes, 6 volts	GE30A/T24/7
Radius of curvature of spherical mirror	69.05 cm
Diameter of spherical mirror	5.568 cm
Diameter of plane mirror	4.22 cm
Diameter of aperture	1.132 mm
Area of aperture	1.006 mm^2
Tan of angle/2 of light spread, calc.	0.04031
Tan of angle/2 of light spread, meas.	0.04021

The light from the lamp passes through the 1.75-inch-diameter tube, strikes the spherical mirror, is reflected to the plane mirror, is reflected to the aperture into the light filter holder, and then passes out of the photometer box to the phototube. Figure 2 shows the phototube in place at the end of the light-tight connecting tube. The phototube could be mounted at 120.7 cm from the aperture so that 74 cm^2 of its face was illuminated, or it could be mounted directly to the photometry box with its face 30.7 cm from the aperture with 4.8 cm^2 of its face illuminated by the identical amount of light. Figure 3 shows the equipment used to measure the phototube output. The Variacs shown in Fig. 2 and 3 are used to control the current to the calibration lamp.

FIG. 2. Photometry System.

FIG. 3. Photometry Detection Equipment. Top to
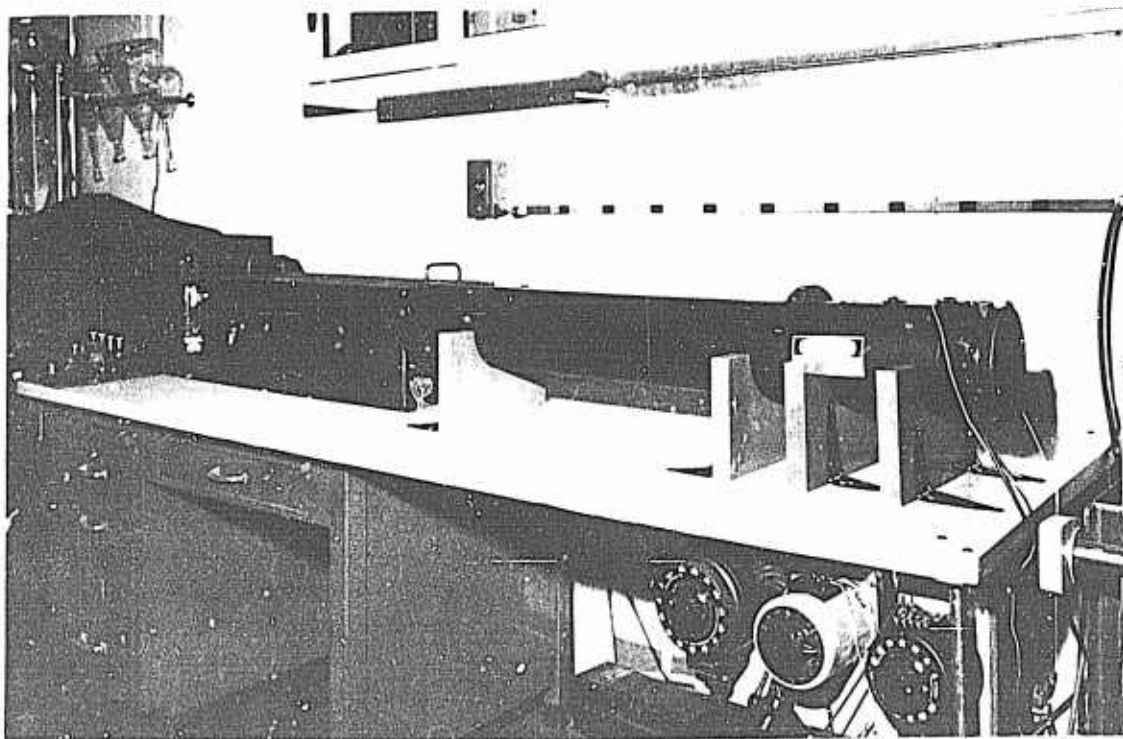bottom: recorder, Keithly Mod. 417 picoammeter,
Radiometer potentiometer (for measuring power
supply stability), and Hamner Model N-401 power
supply.

A working lamp is necessary to limit the time the standard lamp is in operation. The standard lamp cannot be directly replaced in the Mogol bi-post lamp holder by the working lamp, since the lamp filaments have slightly different relative positions. To provide for exact alignment, a microscope with a 3.5-inch working distance was aligned upon the tungsten ribbon by means of a right-angle prism glued to the objective piece. By running the microscope up and down, the vertical alignment of the filament could be checked. By using the 10-power reticle of the microscope, the exact distance of the filament from the spherical mirror could be repositioned. By focusing upon the opening of the aperture with a second microscope, the exact image point of an indicator at the lamp position could be used to place the distance of the indicator at the radial distance of the spherical mirror. By focusing the first microscope on the indicator point, it was then possible to place the filament of any lamp at the correct lamp position where the image of the filament is exactly at the face of the aperture. The 10-power microscope mounting was fixed so that the microscope could be removed when the lamp was in use, yet could also be replaced to its previous alignment. A calibrated Westinghouse type PA 161 AC Ammeter was used to measure the lamp current to 0.1 ampere.

Optics Technology, Inc. (Belmont, California) Spectracoat Monopass filters with neutral density filters were used to select the various portions of the lamp spectral output. The remainder of the equipment and chemicals were described in previous reports (Ref. 1, 5, and 6).

RESULTS

CALIBRATION OF WORKING LAMP

The spectral calibration of standard lamp U-231 from the National Bureau of Standards, is given below.

Spectral Radiance in µw (Steradian-nm-mm^2 of Source)$^{-1}$ for Lamp U-231 at 35 amp

Wavelength, nm	Radiance
300	0.243
320	0.550
350	1.52
370	2.68
400	5.47
450	13.4
500	26.8
550	44.2
600	63.9
650	85.0
700	105.0
750	123.0

The conversion of the standard lamp output from microwatts to photon sec^{-1} was made by Eq. 6.

$$\frac{(\mu w) \times \lambda \times 10^{11}}{19.86} = photon\ sec^{-1} \tag{6}$$

where λ = wavelength in nanometers ($m\mu$). The converted value of the spectral radiance of the standard lamp is given in Fig. 4.

The spectral radiant flux, F, in photon sec^{-1} per nanometer was calculated by the equation:

$$F_\lambda = M_\lambda\ (radiance)_\lambda\ cB/d^2 \tag{7}$$

where M_λ is the reflectance of the combination of mirrors, c is the aperture area in mm^2, B is the area of the spherical mirror, and d is the distance of the spherical mirror from the aperture. Using a 92% reflectance for each mirror and the data from page 4,

$$F_\lambda = 4.35 \times (radiance)_\lambda \times 10^{-3} \tag{8}$$

The combination of Eq. 8 and Fig. 4 permits the determination of the amount of energy passing into the filter box through the $1\text{-}mm^2$ aperture from the standard lamp.

Since the standard lamp is seldom used, its spectral relationship to the working lamp must be determined. This relationship depends upon the ability to substitute one lamp for the other. Table 1 shows a comparison of the measurement of this relationship over the spectral range of 400 to 700 nm.

TABLE 1. Ratio Working Lamp/Standard Lamp Output

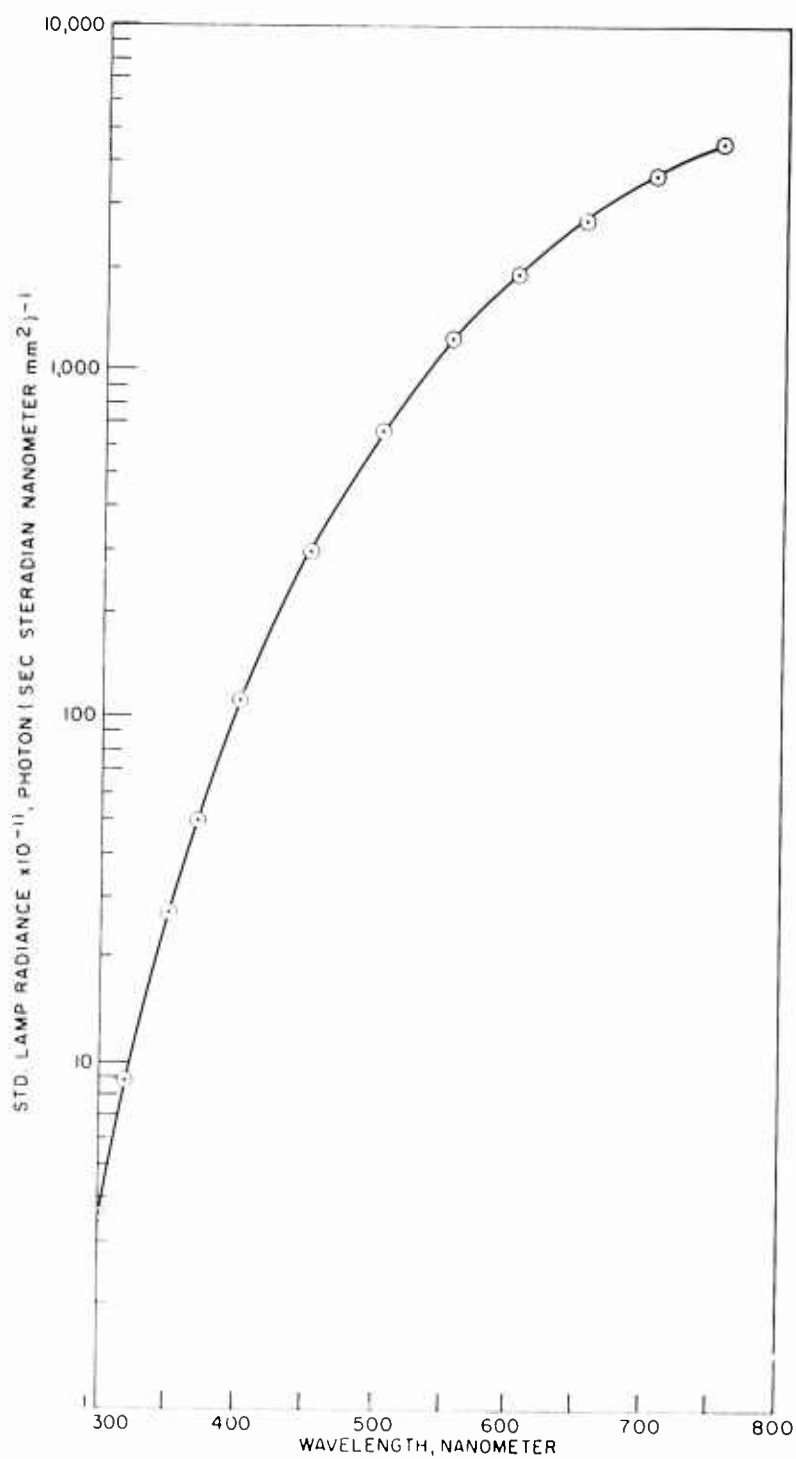| Wavelength of filter, max. nm	January 1964	December 1964	October 1965	Average
416	0.85	0.88	0.86	0.86
450	0.87	0.87	0.85	0.86
485	0.91	0.88	0.83	0.87
518	0.88	0.87	0.87	0.87
551	0.87	0.89	0.89	0.88
585	0.88	0.90	0.87	0.88
615	0.90	0.90	0.91	0.90
645	0.90	0.91	0.91	0.91
685	0.88	0.90	0.93	0.90
715	0.91	0.88	0.89	0.89
Average	0.89	0.89	0.88	0.88

FIG. 4. Spectral Radiance Curve of
Standard Lamp U-231 in photon sec^{-1}.
(Steradian-nanometer-mm^2 of source
at 35 amperes)$^{-1}$.

From Table 1, it can be seen that the working lamp is running slightly colder than the standard lamp, and that it has not had any appreciable change in its output over a 2-year period. Equation 8 can now be modified for calibration of the phototube with the working lamp.

$$F_\lambda \ (W.L.) = 4.35 \times 0.88 \times (radiance) \times 10^{-3}$$

$$F_\lambda \ (W.L.) = 3.83 \times (radiance) \times 10^{-3} \ photon \ sec^{-1} \ nm^{-1} \qquad (9)$$

CALIBRATION OF THE PHOTOTUBE

The energy at the aperture with a single Monopass filter was still too high for the calibration of a phototube. This energy could have been reduced by using a smaller aperture, but additional errors involved with measuring the diameter of small holes would have been introduced. Furthermore, with a small aperture, every speck of dust makes a proportionally larger error. It was therefore decided to use neutral density filters to attenuate the light beam in the filter box. In the course of working with a combination of two Monopass filters and a neutral density filter, it was observed that the order of placing the filters changed the photometric readings. Examination of the band pass of the combinations with the Beckman DK-2 spectrophotometer revealed that the band pass changed with the order of the filters. After consideration of this phenomenon, it was realized that since the Monopass filters had highly reflective surfaces, any two in series would serve as a light trap where they would reflect (and transmit) the light in a manner that depended upon the position and range of the filters. This made it obvious that the filters must be calibrated by a spectrophotometer in the exact position and order of their usage in the photometry box.

The calibration of the filters involved measuring the absorbance of a 1/100 attenuation filter by means of the 0-10% transmission range of the spectrophotometer. Then using the 1/100 filter in the reference beam, the combination of the Monopass filter and a 1/1000 attenuation filter was measured. The attenuation filters, of course, were not perfectly neutral so that it was necessary to have a different correction value for each point of measurement. The use of an attenuation filter in the reference beam of a double-beam-ratio-recording spectrophotometer to extend its range of measurement is shown as follows:

When the instrument is set at 0 and 100% with air in both beams, then the light intensity in the reference beam, I_r, is equal to the intensity of the sample beam, I_s, and the instrument reading, R,

is a transmittance of 1.0. When the reference attenuation filter is placed in the sample beam, then

$$R_o = \frac{I_{so}}{I_{ro}} \tag{10}$$

When the system to be measured is placed in the sample beam and the reference attenuation filter is placed in the reference beam,

$$R_1 = \frac{I_{s1}}{I_{r1}} \tag{11}$$

but

$$I_{r1} = R_o \times I_{ro} \tag{12}$$

so that

$$R_1 = \frac{I_{s1}}{R_o I_{ro}} \tag{13}$$

therefore, the transmittance of the sample system, T_{s1}, is

$$T_{s1} = \frac{I_{s1}}{I_{ro}} = R_o R_1 \tag{14}$$

Since the Beckman DK-2 has an increased sensitivity range for the photomultiplier, the usage of high attenuation did not require the opening of the slits to unworkable values. Since this part of the calibration was rather lengthy, an example of the measurement of the transmittance of a single filter combination is shown in Table 2. Also included in Table 2 is the multiplication of the transmittance times the radiance of Fig. 4 to give F_λ (W.L.)

Values of F_λ (W.L.) were plotted as a function of wavelength so that the total photons per sec could be determined by integration of the curves. Since the maximum values of the F_λ (W.L.) curves were not always the same as those of the transmittance of the filters, these values as well as other parameters of the curves for ten filters are shown in Table 3.

From the results of Table 3, it is now possible to calibrate a phototube. Since the special sensitivity and the over-all sensitivity may vary across the face of a phototube, it is necessary to evaluate this effect. This variation would not be a problem if the chemiluminescent source emitted a uniform radiation on the phototube face. Since the light is from a hemisphere (Ref. 1), there will be a higher light intensity at the center of the phototube than at the edges. Another problem is the direct coupling of the phototube to the light source.

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TABLE 2. Transmittance, T, and Uncorrected[a] Flux
of Working Lamp Through Filter No. 6 with
Maximum Transmission at 485 nm

Wave-length, nm	Reference filter $\times 10^2$, T	Recorded $T \times 10^2$	True $T \times 10^4$	Radiance of lamp $\times 10^{-11}$	Uncorrected[a] F_λ (W.L.) $\times 10^{-9}$
425	1.15	0.20	0.23	190	0.437
430	1.15	0.25	0.29	210	0.609
440	1.13	0.35	0.39	250	0.975
450	1.10	0.48	0.53	300	1.59
460	1.09	0.75	0.82	350	2.87
470	1.07	1.40	1.50	415	6.23
475	1.07	2.10	2.23	460	10.26
480	1.07	3.00	3.18	480	15.26
485	1.05	3.72	3.91	510	19.94
490	1.05	3.10	3.25	535	17.39
493	1.04	2.50	2.61	600	15.66
495	1.04	2.00	2.08	610	12.69
500	1.04	1.10	1.14	630	7.18
510	1.03	0.60	0.62	725	4.50
540	1.00	0.12	0.12	1,010	1.21

[a] Values need to be multiplied by 3.83×10^{-3} of Eq. 9 to give corrected values.

TABLE 3. Calculated Values of Energy in photon sec^{-1}
Passed Through Filter System for Working
Lamp at 35.0 amp

Wavelength of filter, max. nm	λ, energy max. nm	Energy band spread at 1/2 intensity, nm	$\int F_\lambda$ (W.L.)d(nm) $\times 10^{-8}$, photon sec^{-1}	Filter no.
416	418	18	3.05	1
450	455	23	14.5	2
485	485	25	25.1	3
518	518	30	57.4	4
551	557	21	67.5	5
585	585	20	98.0	6
615	615	40	168.	7
645	655	39	168.	8
685	690	40	189.	9
715	720	45	247.	10

Since a semitransparent cathode is used, it is possible for light to be reflected out of the phototube, back through the cathode, and then off the back wall of the light source into the photomultiplier again. Since the calibration with the lamp would not account for a reflection back into the phototube, this effect was evaluated by placing a mask with symmetrically placed holes over the face of the phototube. One side of the mask was black while the other side was a bright aluminum surface. It was found that the ratio of response of black to bright was 1.03, which is within experimental error. Thus there is negligible effects from reflection from the phototube into the flow cell and back into the phototube.

The effect of spectral variation and over-all sensitivity is seen in the results of Table 4, as well as the time variation in response of the phototube, R_λ, used for the calculation of the CQY of TMAE. One of the obvious features of Table 4 is the steady increase in the phototube response. As shown, this amounts to 8.6% per month over a 10-month period. The rapid drop following this increase was probably due to the effect of a series of tests that involved changing the temperature of the cathode of the phototube from 5 to 45°C. This variation is shown in Fig. 5. The change in phototube response with time, of course, limits the accuracy of the measurements. Also to be noted is the decrease in response when all of the light is measured at the center of the phototube rather than spread over its face. This effect is opposite to that seen for three other phototubes of the type used for this work. They all had an increase in sensitivity when the light was received at the center of the tube. This increase is to be expected with a 5-inch-diameter tube since the electrons have a shorter path to the first diode from the center of the phototube compared to the path from the edges. Table 4 also demonstrates that there is no significant shift in the proportion of the spectral sensitivity with time. The sensitivity of the low end of the spectrum increases in the same proportion to the high end. The lack of this type of shift is also noted between the center response vs. total face response.

DETERMINATION OF EMISSION SPECTRA OF TMAE

To make use of the spectral sensitivity of the phototube, it is necessary to know the true spectral emission curve of TMAE. For this type of measurement only relative light intensities on a photon basis are needed. For this work, the emission from several concentrations of TMAE in n-decane were examined. Oxygen pressure was held at 300 torr and the n-octanol concentration was 0.018 $\underline{M}$. The sample was in the flow system (Ref. 1) in a 6-ft, 8-mm O.D. tube bent into a U-shape that was directly in line with the entrance slit of a Bausch and Lomb 50-cm monochrometer. The tube was vacuum jacketed and silvered on the outside. The entrance slit was in line with both of the arms of the U-tube when the slit was open to 20 mm in height. A slit width of 1 mm

TABLE 4. Phototube No. 4 Response, R_λ, as a Function of Time and Area of Exposure

Date		1/2/65	1/5/65	1/5/65	2/12/65	3/8/65	8/12/65	8/12/65	10/2/65	10/3/65	1/21/66	1/21/66
Day no.		2	5	5	43	67	224	224	275	276	386	386
Area, cm²		121	121	4.8	4.8	121	121	4.8	121	121	121	4.8
Filter no.	Photon max., nm				$R_\lambda \times 10^{17}$ amp/(photon sec^{-1}) for applied potential of 836 volts							
1	416	16.4	16.7	15.1	18.4	22.0	25.9	24.6	29.5	29.8	26.2	24.3
2	450	10.7	11.1	10.2	12.6	13.9	16.9	16.8	20.0	19.3	15.9	15.0
3	485	8.30	8.58	8.14	9.74	10.4	12.8	13.1	15.2	14.0	12.2	12.2
4	518	5.23	5.23	4.97	6.10	6.45	8.19	8.71	9.76	9.59	7.14	6.97
5	551	2.98	2.90	2.83	3.53	3.68	4.74	5.18	6.22	5.78	3.85	2.50
6	585	1.50	1.43	1.34	1.66	1.84	2.55	2.68	3.57	3.01	1.94	1.87
7	615	0.530	0.506	0.417	0.524	0.632	0.834	0.815	0.983	0.983	0.708	0.649
8	645	0.190	0.184	0.143	0.184	0.244	0.309	0.280	0.374	0.363	0.286	0.238
9	685	0.0598	0.054	0.041	0.056	0.073	0.094	0.082	0.113	0.111	0.0862	0.0677
10	715	0.020	0.018	0.014	0.019	0.023	0.032	0.028	0.037	0.034	0.0283	0.0214
$\bar{J}_\lambda$[a]	...	0.972	1.000	1.149	0.909	0.784	0.612	0.627	0.506	0.531	0.688	0.732

[a] $\bar{J}_\lambda = \frac{1}{n} \Sigma R(JAN)_\lambda / R_\lambda$ where n = 10.

was used for both entrance and exit, which gave a spectral slit width
of 3.3 nm. A Du Mont K1927, S-20 response phototube was used as the
detection unit. The spectrophotometric unit was calibrated by
measuring the response when light from the working lamp was directly
emitted into the entrance slit at the same setting as above. The
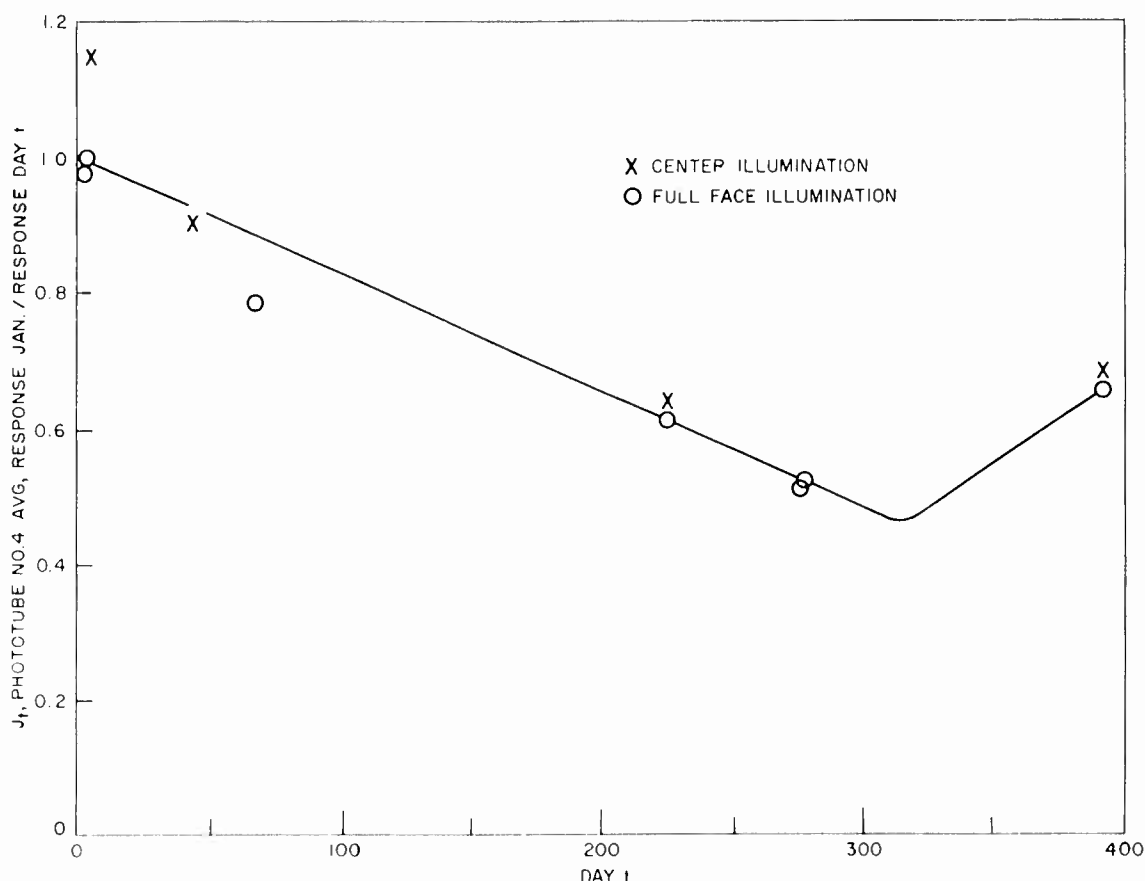relative calibration curve is given in Table 5.

FIG. 5. Variation in Phototube No. 4 Response With Time.

Curves of the measured photomultiplier currents (PMC) under spectro-
photometric conditions identical to those of the calibration are seen
in Fig. 6 and the true curves corrected by the data of Table 5 are shown
in Fig. 7. Also shown in these figures are the curves for TMAE when
excited by a 366-nm mercury line. As can be seen in Fig. 6, the results
of the second-order region of the grating can be found beyond 700 nm.
When a Corning glass filter No. C.S. 2-64 passing only infrared was
placed in front of the phototube, the curve in the second-order region
was not observed.

TABLE 5. Relative photon sec^{-1} amp^{-1} nm^{-1}
Response Calibration for Bausch
and Lomb Monochrometer

Wavelength, nm	Relative response	Wavelength, nm	Relative response
380	0.52	545	2.210
390	0.525	550	2.365
400	0.564	555	2.462
405	0.600	560	2.577
410	0.604	565	2.788
415	0.615	570	2.921
420	0.623	575	3.098
425	0.655	580	3.240
430	0.700	585	3.400
435	0.734	590	3.653
440	0.735	595	3.854
445	0.800	600	4.042
450	0.811	610	4.64
455	0.846	620	5.23
460	0.900	630	6.15
465	0.929	640	6.84
470	1.00	650	7.12
475	1.095	660	8.11
480	1.136	670	9.70
485	1.17	680	11.16
490	1.234	690	13.25
495	1.29	700	18.39
500	1.347	710	19.55
505	1.44	720	21.46
510	1.445	730	26.06
515	1.64	740	32.96
520	1.667	750	41.80
525	1.83	760	54.54
530	1.894	770	69.0
535	2.019	780	86.2
540	2.096	...	......
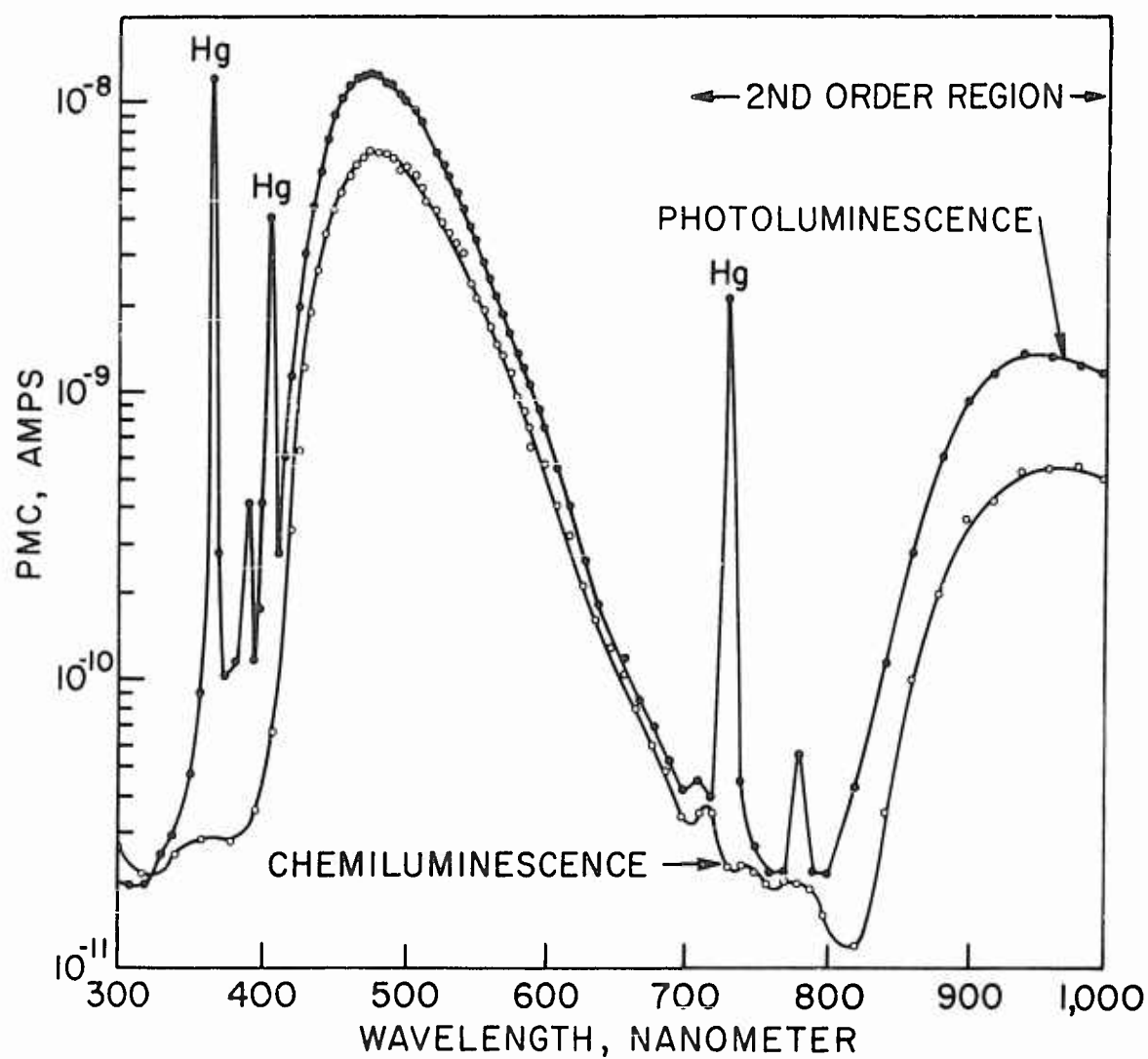
FIG. 6. Uncorrected Chemiluminescence Emission Spectra.
TMAE at 1.4×10^{-3} $\underline{M}$ for photoluminescence. TMAE at
4.5×10^{-2} $\underline{M}$, P_{O_2} at 300 torr, and 1-octanol at $1.8 \times$
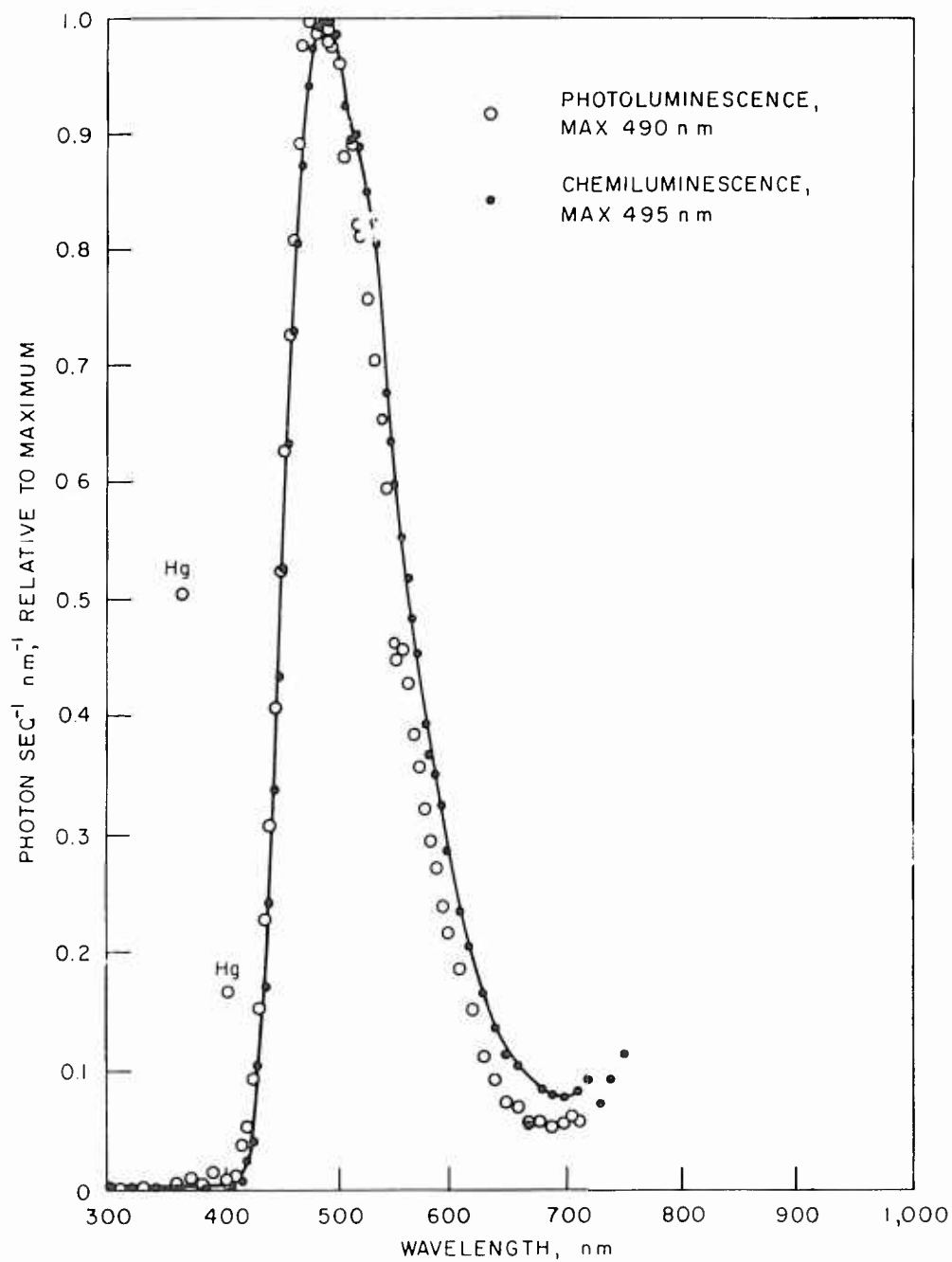10^{-2} $\underline{M}$ for chemiluminescence.

FIG. 7. Corrected Chemiluminescence Emission Spectra.

DETERMINATION OF PHOTOTUBE NO. 4 RESPONSE

By the integration of Fig. 7, a normalizing function for the light emission may be determined:

$$\int_{\lambda \text{ min}}^{\lambda \text{ max}} h_\lambda d\lambda = 119 \text{ nm} \tag{15}$$

where h_λ is the height of the emission curve at wavelength λ.

Then if

$$P_\lambda = \frac{h_\lambda}{119} \text{ nm}^{-1} \tag{16}$$

then

$$\int_0^\infty P_\lambda d\lambda = 1 \tag{17}$$

Taking the phototube calibration, C_λ, to be the reciprocal of the phototube response,

$$C_\lambda = 1/R_\lambda \text{ photor. sec}^{-1} \text{ amp}^{-1} \tag{18}$$

Values of C_λ, are calculated from Table 4 and a plot of values for January and October 1965 are shown in Fig. 8. Although the sensitivity of the phototube has changed, Fig. 8 indicates that the relative wavelength response is about the same. Knowing C_λ and P_λ, it is possible to calibrate the phototube specific to the emission of TMAE,

$$\int C_\lambda P_\lambda d\lambda = K_t \text{ photon sec}^{-1} \text{ amp}^{-1} \tag{19}$$

where K_t represents the phototube response constant specific to the emission of TMAE at time t. The values of $C_\lambda P_\lambda$ as a function of λ for the January 1965 calibration of Table 4 is shown in Fig. 9 where a value of 0.518×10^{17} photon sec^{-1} amp^{-1} was obtained for K_{JAN}. Although Fig. 9 is specific to the calibration in January, the calibration can be extrapolated to other periods by means of Fig. 5.

Thus, since

$$R_\lambda(t_2)/R_\lambda(t_1) = C_\lambda(t_1)/C_\lambda(t_2) = \text{constant} = J_{t\lambda} \tag{20}$$
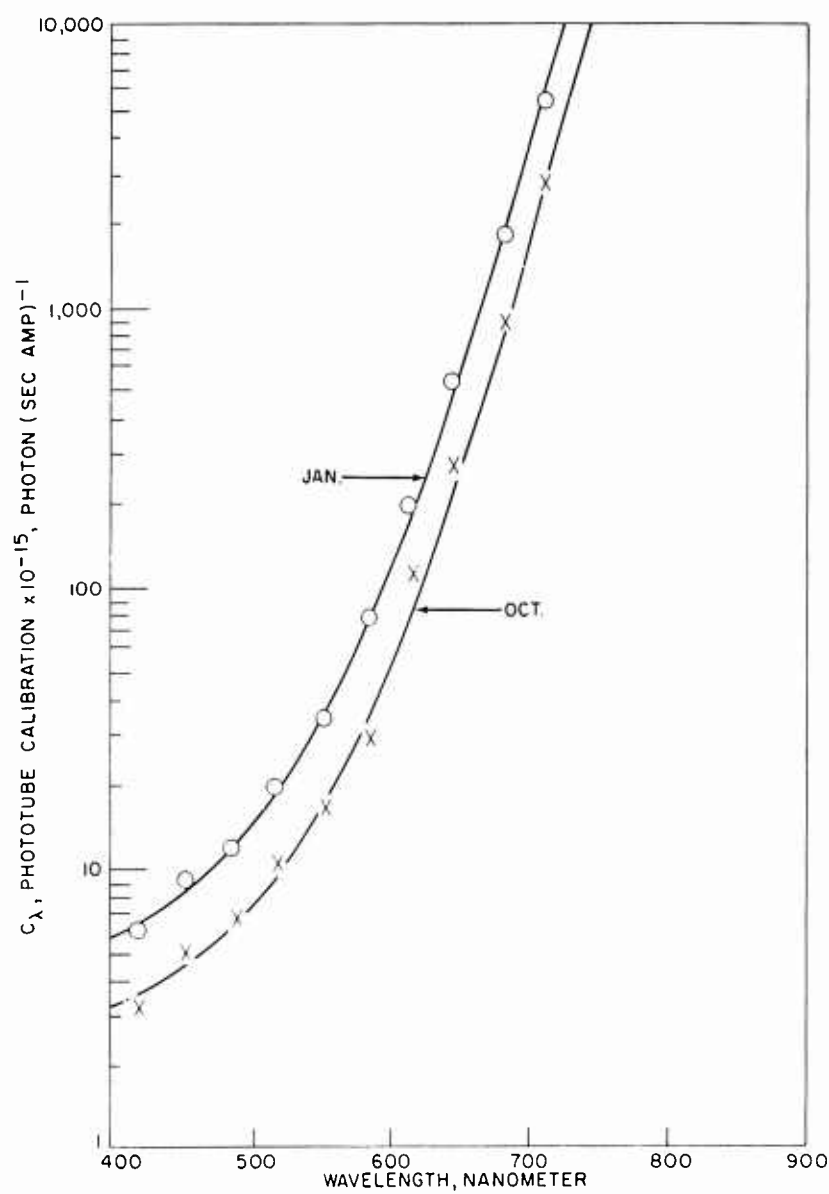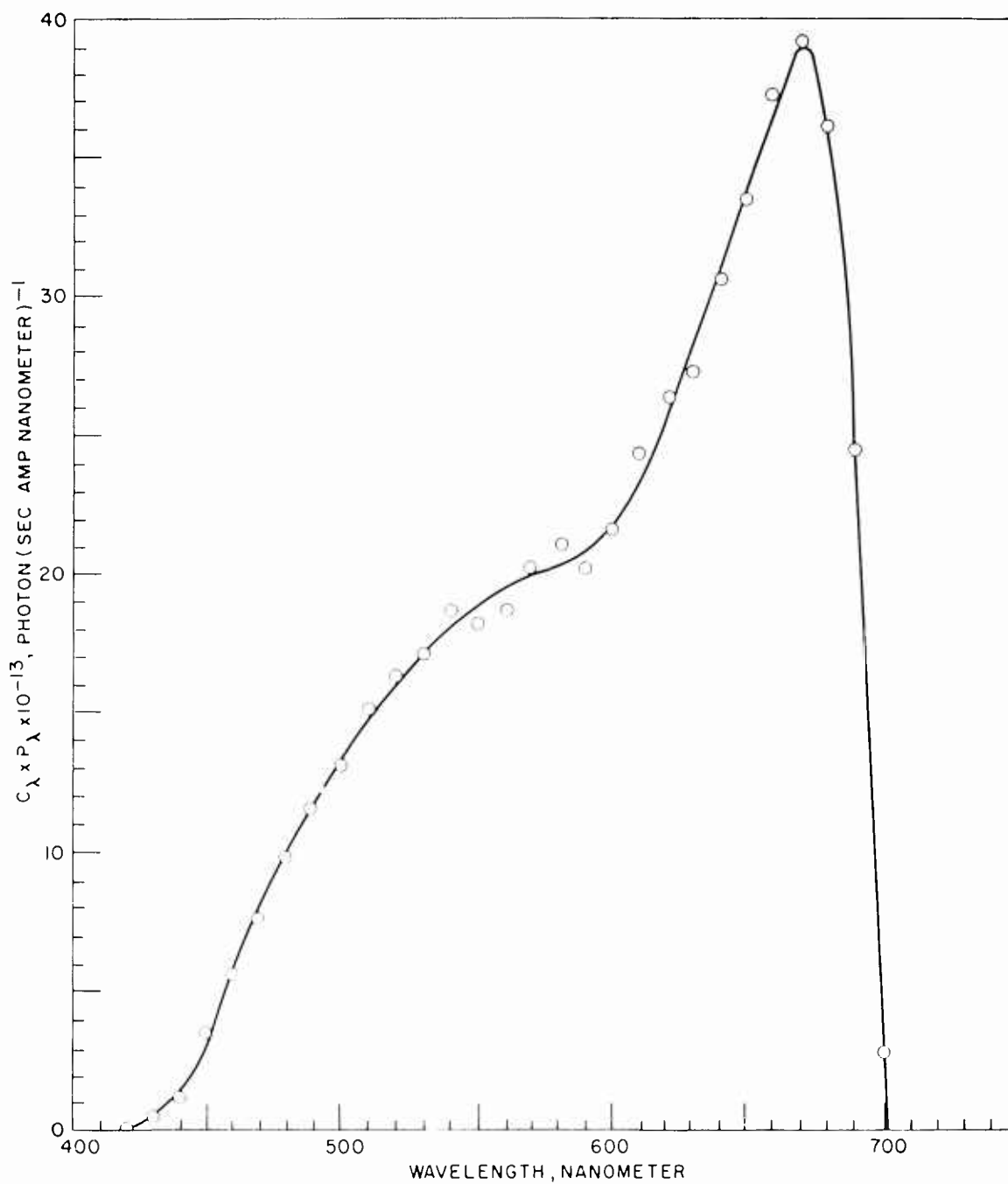
FIG. 8. Phototube Calibration Curves.

FIG. 9. Determination of $\int C_\lambda P_\lambda d\lambda$.

then using average values of J_λ given in Table 4,

$$K_t = 0.518 \times \bar{J}_t \times 10^{17} \text{ photon sec}^{-1} \text{ amp}^{-1} \tag{21}$$

or dividing by Avogadro's number

$$K_t = 0.518 \bar{J}_t \times 10^{17}/6.02 \times 10^{23}$$

$$= 8.6 \bar{J}_t \times 10^{-8} \text{ einstein sec}^{-1} \text{ amp}^{-1} \tag{22}$$

VARIATION OF PHOTOTUBE NO. 4 RESPONSE WITH APPLIED VOLTAGE

The preceding calculations were based upon a reference voltage of 836 applied to the phototube. To expand the range of measurable light intensities, the applied voltage was varied with the light held constant. Examples of this variation are shown in Table 6. Here, there appears to be no significant change in V, current at 836 volts/current at indicated voltage, with time at the lower voltages. The two higher voltages do show some increase in sensitivity after the results for March. Thus Eq. 22 should be modified where voltages other than standard are used:

$$K_t = 8.6 V_i \bar{J}_t \times 10^{-8} \text{ einstein sec}^{-1} \text{ amp}^{-1} \tag{23}$$

TABLE 6. Variation of Phototube Response
With Applied Voltage Ratio V^a

Date	419.3 V	585.6 V	1086.8 V	1339.0 V
1/2/65	62.3	8.90	0.170	0.0290
1/2/65	··	8.41	0.177	0.0306
1/2/65	66.6	9.83	0.171	0.0281
1/3/65	65.0	9.07	0.175	0.0289
1/4/65	51.5	9.12	0.173	0.0294
1/5/65	64.9	9.09	0.175	0.0291
2/12/65	64.4	9.10	0.171	0.0254
3/9/65	60.9	9.33	0.172	0.0246
8/12/65	66.0	8.97	0.151	0.0125
8/13/65	69.3	9.17	0.158	0.0117
10/1/65	67.4	9.09	0.154	····
10/2/65	64.9	8.70	0.169	0.0183
Average	63.9	9.07	0.168	0.0243

[a] V = current at 836 volts/current at indicated voltage.

DETERMINATION OF ABSOLUTE LIGHT EMISSION AT LOW CONCENTRATIONS OF TMAE

Equations 3-5 describe the Stern-Volmer quenching terms needed to evaluate Eq. 1 and 2. The rate of autoxidation of TMAE was shown to be (Ref. 6)

$$- \frac{d(TMAE)}{dt} = E \cdot O_2 \cdot F(A) \text{ mole liter}^{-1} \text{ sec}^{-1} \tag{24}$$

where F(A) is a function only of the alcohol concentration and can be determined by semilog plots of E vs. time:

$$\frac{d \ln E}{dt} \times \frac{1}{O_2} = F(A) \text{ torr}^{-1} \text{ sec}^{-1} \tag{25}$$

Equations 3-5, 24, and 25 cover all of the variable parameters in I, except ϕ_c. Because the light was shown to be second order in TMAE concentration (Ref. 1 and 3), ϕ_c must be proportioned to the TMAE concentration at low concentration of TMAE (Ref. 7). Now using Eq. 1

$$I = \frac{L \times E \times EO_2 F(A)}{1 + \Sigma K_i [Q_i]} \text{ einstein liter}^{-1} \text{ sec}^{-1} \tag{26}$$

where L represents all of the desired constants. By means of Eq. 27 it is possible to determine I through measurement of the photomultiplier current at the reference voltage (PMCF), from the 128-ml-light-emission flow cell (Ref. 1),

$$I = \frac{\bar{J}_t \times V_i \times K \times PMCi}{0.128} \tag{27}$$

$$I = 6.72 \bar{J}_t \times PMCF \times 10^{-7} \text{ einstein liter}^{-1} \text{ sec}^{-1} \tag{28}$$

or

$$L = 6.72 \bar{J}_t \times \frac{PMCF}{E^2} \times \frac{[1 + \Sigma K_i (Q_i)]}{O_2 \times F(A)} \times 10^{-7} = \text{constant} \tag{29}$$

The constant L, supplies the quantitative link between the parameters of light quenching, the efficiency of formation of excited TMAE molecules, and the rate of reaction of TMAE. It allows the determination of the CQY at other than single concentrations of the reactants as have been previously reported (Ref. 2 and 3). Through determination of the photomultiplier current as a function of the TMAE concentration for known constant oxygen pressures and known constant 1-octanol concentrations, values of L can be determined. Table 7 shows the experimental conditions while Table 8 shows the values which were calculated from the experimental results from days 60 to 382. The average value of L was

TABLE 7. Conditions for 30°C Quantum Yield Measurements

Run no.	Day no.	1-Octanol conc. $\times 10^3$, $\underline{M}$.			P_{O_2}, torr	Initial $E \times 10^4$, $\underline{M}$	Time duration, sec	n
		A_0	A_1	A_4				
1	60	8.49	8.49	0.003	700	3.4	1.4×10^5	4
2	63	13.9	13.9	0.026	700	3.1	8.6×10^4	3
3	250	25.0	24.0	0.26	712	3.4	5.5×10^3	14
4	251	25.0	24.0	0.26	1,407	5.8	8.3×10^3	17
5	361	7.3	7.3	0.002	800	3.0	7.9×10^4	5
6	370	21.0	20.8	0.11	1,400	3.7	1.1×10^4	6
7	373	35.8	32.8	0.75	708	2.5	2.2×10^3	9
8	374	35.8	32.8	0.75	1,400	2.9	1.4×10^3	12
9	377	50.0	40.8	2.3	700	2.0	1.4×10^3	11
10	377	50.0	40.8	2.3	1,400	2.4	1.4×10^3	9
11	378	207.8	79.8	32.0	58.1	1.8	7.0×10^2	11
12	378	207.8	79.8	32.0	162.0	0.2	2.0×10^2	3
13	380	575.	115.	115.	23.2	3.7	1.5×10^3	5
14	381	575.	115.	115.	118.7	0.4	1.0×10^2	6
15	382	961.	121.	210.	20.7	1.4	6.0×10^2	10
16	382	961.	121.	210.	44.1	0.4	9.0×10^1	5

TABLE 8. Results of 30°C Quantum Yield Measurements

Run no.	$\dfrac{PMCF}{E^2}$	$1 + K_i[Q_i]$	$F(A)$, torr sec^{-1}	J_t	L, einstein mole^{-2} liter
1	0.122[a]	60.9	9.20×10^{-9}	0.78	0.61
2	0.387[a]	61.2	3.02×10^{-8}	0.78	0.59
3	2.54	62.9	2.09×10^{-7}	0.56	0.40
4	2.50	122.0	1.98×10^{-7}	0.56	0.41
5	0.154	69.4	9.17×10^{-9}	0.56	0.55
6	1.27	121.	9.36×10^{-8}	0.62	0.45
7	5.89	63.5	5.01×10^{-7}	0.64	0.45
8	5.83	122.	5.28×10^{-7}	0.64	0.41
9	11.5	64.9	1.25×10^{-6}	0.66	0.38
10	12.9	124.	1.26×10^{-6}	0.66	0.41
11	44.0	43.0	4.47×10^{-5}	0.67	0.33
12	75.5	51.9	2.97×10^{-5}	0.67	0.37
13	9.14	128.	9.5×10^{-5}	0.68	0.24
14	108.8	136.	1.56×10^{-4}	0.68	0.37
15	5.75	227.	1.55×10^{-4}	0.69	0.19
16	33.3	229.	1.43×10^{-4}	0.69	0.56
Average					0.42 ± 0.03

[a] PMCF calculated through use of V.

found to be 0.42 einstein mole^{-2} liter with an estimated standard deviation of the mean of 0.03. The estimated standard deviation for an individual run was 0.12. These deviations were not weighted by considering the number of values of PMCF/E^2, n, which were used on one day to determine L.

A value for L can also be calculated from the quenching data work (Ref. 4). The value of 1/C in that report of 1.83×10^{-6} amp^{-1} yields a value of L of 0.37 einstein mole^{-2} liter. This work was performed on days 12-34 so a value of $\bar{J}_t$ of 1.0 was used in this evaluation.

The quenching work was performed with silicone grease as the seal between the light emission flow cell and the phototube. This causes a small region where light could be trapped because silicone grease has an index of refraction (1.41) lower than that of pyrex (1.474) and the glass of the phototube (1.50). For the present work a glycerol seal was used with an index of refraction of 1.473. Apparently only a slight increase occurred by using the glycerol seal.

It should be noted that the high values for L at low alcohol concentration may be due to enhanced light output from the unevaluated effects of the glass walls. There are a number of right-angle bends that have been painted black and also Teflon inserts at ball-joint connections that help to insulate the flow cell from the light produced in the rest of the system. It is believed that the effect of light piping is compensated by the 3% light loss due to a single reflection from a silver surface. It is estimated that the light-emission-flow-cell emits $100 \pm 5\%$ of the light produced within the cell and that the over-all absolute quantum yield measurements are accurate to at least $\pm 20\%$ of the reported value.

DETERMINATION OF LIGHT EMISSION AT HIGH CONCENTRATIONS OF TMAE

The absolute light intensity measurements were made at low TMAE concentrations where it was possible to make measurements involving rapid rates of reaction and yet have the solution in equilibrium with the oxygen in the gas phase. At high TMAE concentrations the reaction rates are limited to slower rates, since consumption of only small percentages of the total amount of TMAE can otherwise result in oxygen depletion of the solution. Since the light intensity at high TMAE concentrations was more than could be measured with the 128-ml-light-emission flow cell, the equipment used to measure the emission spectra of TMAE was used.

The concentration of the alcohol was determined through its adsorption at 1.405 microns. The value of F(A) was evaluated (Ref. 9) as a function of A_1 and found to be

$$F(A) = 1.0 \times 10^{-9} + 4.6\ A_1 \times 10^{-7} + 0.75\ A_1^4 \qquad (30)$$

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F(A) was calculated by means of Eq. 30, since its values could not be determined experimentally at such high TMAE concentrations. The latter fact is due not only to the oxygen depletion effect, but also to the "loss" of alcohol monomer whenever very much TMAE has reacted. This loss was shown to be due to complexing of the alcohol monomer by tetramethylurea (Ref. 10), which is a major reaction product (Ref. 11). Since the predicted reaction kinetics from a "working mechanism" (Ref. 12) indicated the possibility of a TMAE concentration term in the denominator of ϕ_c, the light emission measured by the PMC was evaluated as follows through rearrangement of Eq. 26 with the oxygen held constant at 760 torr and over-all constant quenching terms.

$$\frac{E^2 \; F(A)}{PMCF} = a + bE \tag{31}$$

For TMAE 10^{-3} $\underline{M}$ and lower, bE was not measurable, Table 9 indicates the results of experimental measurements with TMAE as high as 0.22 $\underline{M}$. A least-squares evaluation yields an intercept, a, of 0.0193 and a slope, b, of 0.222. By dividing the slope by the intercept, the effects of the quenching and other terms may be removed since the left-hand expression contains all terms found for low TMAE runs.

$$\frac{E^2 \; F(A)}{a \; PMCF} = 1 + 11.5 \; E \tag{32}$$

Thus, making use of the value of 0.42 einstein mole^{-1} for L, Eq. 26 for low TMAE, and Eq. 32 for high TMAE concentrations,

$$I = 0.42 \times \frac{1}{[1 + \Sigma K_i(Q_i)]} \times \frac{E}{[1 + 11.5E]} \times E \cdot P_{O_2} \cdot F(A)$$

$$\text{einstein liter sec}^{-1} \tag{33}$$

TABLE 9. Evaluation of Light Emission at High TMAE Concentrations

$10^2 \times$ TMAE, $\underline{M}$	$10^2 \times A_1$, $\underline{M}$	$10^9 \times F(A)$	$10^{10} \times$ PMCF	$\dfrac{10^3 \times E^2 \; F(A)}{PMCF}$
1.39	1.94	116.	9.28	24.1
2.76	1.94	116.	35.5	24.9
5.55	1.88	104.	107.	30.0
8.20	1.88	104.	210.	33.3
10.8	1.88	104.	280.	43.1
8.3	1.38	34.1	60.1	38.9
10.3	1.38	34.1	82.	43.9
12.3	1.38	34.1	105.	49.2
22.0	1.38	34.1	245.	67.4

DISCUSSION

ABSOLUTE MEASUREMENT OF LIGHT FROM A GLOWING TRANSPARENT OBJECT

When light strikes a boundary going from a medium of high index of refraction, n_2, to a lower one, n_1, a certain proportion is reflected back into the original medium. This amount varies from $(n_2-n_1)^2/(n_2+n_1)^2$ when the light is normal to the surface to total reflection at the critical angle, Ψ_c, or greater

where

$$\sin \Psi_c = n_1/n_2 \tag{34}$$

Depending on the geometry, adsorption of the media, and the indexes of refraction, not only is it difficult to predict the geometry of light distribution that is emitted from a glowing transparent object, but large amounts of light can be permanently "trapped" within the object. As an example, Gillette (Ref. 13) calculates that the light trapped within a rectangular prism with an index of refraction of 1.58 amounts to 32.8% of the total light when the prism is in air. For a sphere it would have been 46.4%. The effect of the absorption of the light that can occur on the multiple passes involved at angles less than critical is not taken into account.

The geometry of the distribution of light has been solved for some special cases. Gardon (Ref. 14) has a solution for a "semi-infinite" body, and Melhuish (Ref. 15) has demonstrated that the emission from a small isotropically emitting source behind an infinite plane surface in a medium of refractive index n_1, follows the relationship predicted by Gilmore, Gibson, and McClure (Ref. 16),

$$I = I_0 n_i^{-1} \cos \Psi \ (n_i^2 - \sin^2\Psi)^{-1/2} \text{ photon cc}^{-2} \text{ sec}^{-1}$$

where Ψ is the angle from the perpendicular to the face. Shepp (Ref. 17) had indicated that the geometry problem for a cylinder was impossible to solve, but Melhuish solved the problem of internal reflectance by painting black all but one of the walls of the cylinder, and by having only a thin portion at the surface emit light.

LIGHT EMISSION FROM THE HEMISPHERICAL FLOW CELL

In the apparatus used for this work, the hemispherical flow cell is coupled directly to the phototube with a small (1.41 to 1.50) increase in the index of refraction upon going from the solution to the cathode of the phototube. The only decrease in the index of refraction occurs where the light passes from the solution into the glass, is reflected

from the silver mirror, and meets the glass (index 1.47)-decane (index 1.41) interface. Even if light were to be trapped between the interface and the silver mirror, it would soon be "piped" into the phototube as the interface is not parallel to the mirror.

CHEMILUMINESCENCE QUANTUM YIELD OF TMAE

Sufficient data are now available to quantitatively determine each term in Eq. 1. Knowing the photochemiluminescence quantum yield, 0.35 ± 0.05 (Ref. 5), the chemiluminescence emission quantum yield must be

$$\phi_e = \frac{0.35}{1 + 48 A_1 + 1040 A_4 + 0.085 P_{O_2}}$$

einstein per mole of excited TMAE　　　　　　　　　　(35)

which leaves through the use of Eq. 1, 33, and 35

$$\phi_c = \frac{1.20 \ E}{1 + 11.5 \ E} \text{ mole excited TMAE per mole of reacted TMAE} \quad (36)$$

For oxygen below 1 torr in 100% TMAE (4.3 $\underline{M}$), ϕ_c would be 0.102, and $\phi_e \phi_c$, the chemiluminescence quantum yield, would be 0.036.

Winberg, Downing, and Coffman (Ref. 2) have reported a CQY of 3×10^{-4} einstein per mole of reacted TMAE for 1 ml of TMAE reacted over water. They obtained this quantum yield by measuring the total light emitted by the TMAE.

Since the cation radical of TMAE quickly colors the water solution, some type of correction must be made for the light absorbed in the water phase as well as a correction for light trapped within the complex geometry of a cylinder of TMAE floating on a cylinder of water all inside a beaker with a silver coat on the outside. If it can be assumed that Winberg et al. had a quantitative measure of the light emitted from their apparatus, then a comparison with the present results can be made. For this calculation it will be assumed that all of the oxidation products are extracted into the water phase and that the TMAE contained a uniform concentration of 158 torr of oxygen. In this case the CQY for 100% TMAE would be lowered by the quenching of the oxygen and would be 2.4×10^{-3} einstein mole^{-1}. The water quenching should not be very important even though water quenches more than 1-octanol (Ref. 3). Our value is 10 times larger than that of Winberg et al.; however, it is not just the physical apparatus which is different. Urry (Ref. 11) has shown that the major reaction products of TMAE in nonpolar media is tetramethylurea and tetramethyloxamide, and the dication of TMAE is the product from reactions over water. The

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quantum yields above would indicate that a major portion of the reaction over water goes through a "dark" nonlight producing step leading to the dication of TMAE as the final product. It would appear that Winberg et al. were evaluating a different reaction than reported here.

Paris completely autoxidized a 0.03 $\underline{M}$ TMAE solution of 2×10^{-3} $\underline{M}$ methanol in cyclohexane. He does not specify the oxygen pressure, but does refer to other tests using 760-torr pressure. If this value is assumed, then it is possible to estimate the light emission from his solution. The quenching effects of the reaction products will only become serious after a major portion of the light has been emitted. The major quencher, tetramethylurea, has a quenching constant of about 400 liter mole^{-1}, so this would add a maximum of 8 to a quenching term of 65.6. So if a time-average quenching term of 70 is used, it will be possible to calculate the total light emitted by his solutions.

$$I = \frac{0.42}{70} \frac{E}{(1 + 11.5 \ E)} \times -\frac{dE}{dt} \tag{37}$$

$$Idt = -6.0 \times 10^{-3} \frac{EdE}{(1 + 11.5 \ E)} \tag{38}$$

$$\int_{o}^{\infty} Idt = -6.0 \times 10^{-3} \times \frac{1}{11.5^2} \ [11.5 \ E - \ln \ (11.5 \ E + 1)] \Big|_{E_o}^{0} \tag{39}$$

$$\int_{o}^{\infty} Idt = 6.0 \times 10^{-3} \frac{11.5 \ E_o - \ln \ (11.5 \ E_o + 1)}{(11.5)^2} \tag{40}$$

Equation 40 may be estimated by expanding the $\ln \ (1 + 11.5 \ E_o)$ where $11.5 \ E_o < 1$

$$\int_{o}^{\infty} Idt = 6.0 \times 10^{-3} \left[E_o^2/2 - \frac{E_o^3}{3 \times 11.5} + \frac{E_o^4}{4 \times 11.5^2} \right]$$

$$= 2.7 \times 10^{-6} \ \text{einstein liter}^{-1} \tag{41}$$

which yields an average quantum yield for 0.03 $\underline{M}$ TMAE of 8.8×10^{-5} einstein mole^{-1}. This yield is higher than the value of 4×10^{-6} reported by Paris. Paris did not state the corrections, if any, that he made for the light transfer from within his reaction vessel to the phototube. Since he had a spherical vessel from which the light had to pass through air to reach the phototube, it must be assumed that he did not correct for light trapped within the system.

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5 AUTHOR(S) (Last name, first name, initial)

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13 ABSTRACT

The chemiluminescence quantum yield for a n-decane solution of tetrakis-(dimethylamino)ethylene (TMAE), oxygen, and 1-octanol at 30°C was determined under a wide range of experimental conditions. It is found that a maximum possible quantum yield of 3.6% can be expected. The yield is found to depend upon TMAE/[11.5(TMAE) + 1] so that it decreases with decreasing TMAE concentration. A discussion is given concerning yields reported by other workers.

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